

IN THE SPECIFICATION:

Please insert the following below the title of the invention:

This application is a division of Application No. 09/839,891, filed April 23, 2001, allowed, which is a division of Application No. 09/266,829, filed March 12, 1999, now U.S. Patent No. 6,303,945.

Please amend the paragraph starting at page 1, line 11, and ending at page 1, line 18, as follows:

Microcrystalline silicon semiconductors have been presented ~~in~~ since 1979. See, e.g., ~~(S. USUI and M. KIKUCHI, "PROPERTIES OF HEAVILY DOPED GD-Si WITH LOW RESISTIVITY", Journal of Non-Crystalline Solids, 34 (1979), pp. 1 to 11 pp. 1 to 11).~~ ~~This article has described that a low-resistivity microcrystalline silicon semiconductor doped with phosphorous was able to be deposited by a glow discharge method.~~

Please amend the paragraph starting at page 2, line 8, and ending at page 2, line 11, as follows:

However, the possibility that such mixed layers of amorphous and microcrystalline silicon could be applied ~~in~~ to semiconductor elements such as solar cells has been suggested, but there has been no actual application.

Please amend the paragraph starting at page 4, line 8, and ending at page 4, line 21, as follows:

When the inventors teamed up a transmission electron microscope with a secondary ion mass spectrometer and searched for the cause of the many defect states in the vicinity of the interfaces ~~mentioned~~ mentioned above, they discovered that the n-type semiconductor layer and the i-type semiconductor layer, or the p-type semiconductor layer and the i-type semiconductor layer were discontinuously stacked. Thus, they assumed that the reason why there were many defect states in the vicinity of the interfaces mentioned above was that the n-type semiconductor layer and the i-type semiconductor layer, or the p-type semiconductor layer and the i-type semiconductor layer were discontinuously stacked.

Please amend the paragraph starting at page 5, line 14, and ending at page 5, line 22, as follows:

When the inventors analyzed transmission electron microscope and X-ray diffraction data, it became clear that structural distortions were liable to be concentrated in the relatively large spaces between microcrystal grains, where there were many defects. These defects will reduce the ~~trans-portability~~ transportability (mobility) of photo-excited free carriers and shorten the ~~life-time~~ lifetime thereof to lower the characteristics of the semiconductor element.

Please amend the paragraph starting at page 7, line 2, and ending at page 7, line 4, as follows:

A third aspect of the present invention is directed to a method of manufacturing a semiconductor element [[,]] comprising the steps of:

Please amend the paragraph starting at page 7, line 16, and ending at page 7, line 18, as follows:

A fourth aspect of the present invention is directed to a method of manufacturing a semiconductor element [[,]] comprising the steps of:

Please amend the paragraph starting at page 8, line 1, and ending at page 8, line 3, as follows:

A fifth aspect of the present invention is directed to a method of manufacturing a semiconductor element [[,]] comprising the steps of:

Please amend the paragraph starting at page 8, line 13, and ending at page 8, line 15, as follows:

A sixth aspect of the present invention is directed to a method of manufacturing a semiconductor element [[,]] comprising the steps of:

Please amend the paragraph starting at page 9, line 8, and ending at page 9, line 16, as follows:

~~An~~ A ninth aspect of the present invention is directed to a method of manufacturing a semiconductor element[[,]] comprising the step of generating a plasma in a gas phase to decompose a source gas, thus forming a semiconductor layer comprising microcrystals on a substrate, wherein an electric power to be applied to the plasma is periodically changed to form a semiconductor layer comprising microcrystal grains of different sizes as a mixture.

Please amend the paragraph starting at page 9, line 17, and ending at page 9, line 25, as follows:

A tenth aspect of the present invention is directed to a method of manufacturing a semiconductor element [[,]] comprising the step of generating a plasma in a gas phase to decompose a source gas, thus forming a semiconductor layer comprising microcrystals on a substrate, wherein a halogen-containing gas is added at regular intervals into the source gas to form a semiconductor layer comprising microcrystal grains of different sizes as a mixture.

Please amend the paragraph starting at page 10, line 22, and ending at page 11, line 1, as follows:

Fig. 6A is a schematic partial sectional view showing a microcrystalline semiconductor layer in which the grain diameters of microcrystal grains are uniform, and Fig. 6B is a schematic partial sectional view showing a microcrystalline semiconductor layer in which the grain diameters of microcrystal grains are different.

Please insert the following paragraph at page 11, before line 3:

Figure 7 is a schematic sectional view showing an example in which a microcrystalline semiconductor layer is deposited on a substrate.

Please amend the paragraph starting at page 12, line 20, and ending at page 14, line 14, as follows:

The present inventors have discovered that in a semiconductor element comprising microcrystalline semiconductors, providing microcrystal grains with different grain diameters as a mixture within the semiconductor layer and providing a semiconductor junction within the microcrystal grains are ~~an~~ effective ~~way~~ ways to solve the above-mentioned problems. In the specification and claims, the expression “a semiconductor layer comprising microcrystal grains of different grain diameters as a mixture” means a semiconductor layer in which microcrystal grains having different grain diameters without any regularity are distributed almost at random. Further, the fact that microcrystal grains with different grain diameters are present as a mixture has been confirmed by calculating the average crystalline grain diameter from the half-width of the X-ray diffraction (220) peak and finding the average crystalline grain diameter from the dark-field image of a transmission electron microscope, and finding that they ~~differed~~ differ by more than 50 Å. In the semiconductor element, by mixing microcrystal grains with different crystal grain diameters, distortions can be made even smaller than when a three dimensional space (semiconductor layer) is filled with microcrystal grains of the same crystalline grain diameters. As a result, it is possible to increase the transportability (mobility) of photo-excited free carriers in the microcrystalline semiconductor layer and to lengthen the ~~life time~~ lifetime of the carriers. Further, in the semiconductor element, at least a portion of each of two semiconductor layers with different electric characteristics (for example, a portion of the n-type semiconductor layer and a portion of the i-type semiconductor layer or a portion of the p-type semiconductor layer and a portion of the i-type semiconductor layer) are formed within the same microcrystal grains in the vicinity of the interface of the two layers. In other words, in the semiconductor element, microcrystal grains are present

extending over two semiconductor layers. Forming a semiconductor junction such as p/i or n/i within microcrystal grains in such a way can reduce the defect states in the vicinity of the interface to a great extent. As a result, declines in the open circuit voltage (Voc), short circuit current (Jsc), and fill factor (FF) of the solar cell are prevented. Further, increase in the series resistance and decline in the shunt resistance of the solar cell are also prevented. As a result, the conversion efficiency of the solar cell is improved.

Please insert the following paragraph at page 17, before line 11:

Fig. 7 is an example in which microcrystalline semiconductor layers 705, 702 and 706 are grown on a substrate 701. The semiconductor layer having the first electric characteristics is the portion 705 below the straight line 703. The semiconductor layer having the second electric characteristics is the portion 702 above the straight line 703 and below the straight line 704. The semiconductor layer having the third electric characteristics is the portion 706 above the straight line 704.

Please amend the paragraph starting at page 17, line 11, and ending at page 18, line 3, as follows:

Fig. 6A is a schematic partial sectional view showing a microcrystalline semiconductor layer in which the grain diameters of microcrystal grains are uniform, and Fig. 6B is a schematic partial sectional view showing a microcrystalline semiconductor layer in which the grain diameters of microcrystal grains are different. In the microcrystalline semiconductor layer of Fig. 6A, since the grain diameters of the microcrystal grains 601 are uniform, an amorphous layer with many defects unfilled by

microcrystal grains ~~are~~ is present in the microcrystalline semiconductor layer. In Fig. 6A, reference numeral 602 designates a space not filled with microcrystals. On the other hand, since the microcrystalline semiconductor layer of ~~fig. 6B~~ Fig. 6B is constituted of microcrystal grains with different grain diameters, there is substantially no space unfilled with microcrystal grains. As a result, the mobility and ~~life-time~~ lifetime of carriers of the microcrystalline semiconductor layer of Fig. 6B will be greater than those of Fig. 6A.

Please amend the paragraph starting at page 23, line 13, and ending at page 23, line 23, as follows:

(1) A crystalline semiconductor layer having first electric characteristics (a doped semiconductor layer), and then a microcrystalline semiconductor layer having second electric characteristics (a non-doped microcrystalline semiconductor layer or a microcrystalline semiconductor layer having a different electric characteristics from the first doped semiconductor layer) is deposited by changing the source gasses under conditions such that microcrystals grow continuously, thus forming the semiconductor junction with the microcrystal grains.

Please amend the paragraph starting at page 23, line 24, and ending at page 24, line 3, as follows:

(2) A crystalline semiconductor layer having first electric characteristics is formed; a microcrystalline or amorphous semiconductor layer having second electric characteristics is formed on the semiconductor layer; and the both semiconductor layers are

annealed at a temperature below the melting points, thus forming a semiconductor junction within the microcrystal grains.

Please amend the paragraph starting at page 27, line 26, and ending at page 28, line 9, as follows:

The average crystal grain diameter of the microcrystal grains ~~are~~ is preferably 100 Å to 1000 Å when obtained by calculation using the Scherrer's equation from the half-width of the X-ray diffraction (220) peak. If the average diameter is determined from the dark field image of a transmission electron microscope, it is preferably within 100 Å to 10 μm. When the average crystal grain diameter of columnar microcrystals is determined using a transmission electron microscope, it is preferred than a geometric mean of the long axis and the short axis thereof is within the above range.

Please amend the paragraph starting at page 28, line 10, and ending at page 29, line 8, as follows:

Further, the preferred proportion of amorphous phase contained in the microcrystalline semiconductor is such that when observed with the Raman spectrum, the ratio of amorphous phase related peaks to crystal phase related peaks is not more than 70%. If the average crystalline grain diameter is less than 100 Å, more amorphous will exist on the crystal grain boundaries and photodeterioration is liable to ~~be occurred~~ occur. Also, if the crystal grain diameter is too small, there is a possibility that the mobility and ~~life-time~~ lifetime of electrons and positive holes may be smaller to lower the characteristics as semiconductor. On the other hand, if the average crystal grain diameter calculated using

the Scherrer's equation is greater than 1000 Å, there is a possibility that relaxation of the crystal grain boundaries may not progress sufficiently, defects such as dangling bonds may arise in the crystal grain boundaries, and the defects may act as recombination centers for electrons or positive holes, whereby the characteristics of the microcrystalline semiconductor may be lowered. As the shape of microcrystals, a shape which is long and thin (columnar) in the direction of movement of the charge is preferred. In addition, the proportion of hydrogen atoms or halogen atoms contained in the microcrystalline semiconductor layer of the present invention is preferably not more than 30%.

Please amend the paragraph starting at page 30, line 5, and ending at page 30, line 13, as follows:

When these materials are applied to doped layers, it is preferable to add a p-type valency controller (Group III atoms of Periodic Table: B, Al, Ga, In, or Tl) or an n-type valency controller (Group V atoms of Periodic Table: P, As, Sb, or Bi) at a high concentration. The ~~contents~~ content of Group III atoms in the p-type semiconductor layer and Group V atoms in the n-type semiconductor layer is preferably 0.1 to 50 atomic %.

Please amend the paragraph starting at page 31, line 21, and ending at page 32, line 6, as follows:

When a multiple-element (alloy) semiconductor layer such as SiC, SeGe, etc., is used, it is preferable that the content of hydrogen atoms and/or halogen atoms is changed in response to the change in content of silicon atoms. In the semiconductor layer, depending on the bandgap, the content of hydrogen atoms and/or halogen atoms is smaller

at a portion of narrow bandgap. Incidentally, it is preferred that the content of the hydrogen atoms and/or halogen atoms at a portion where the content of silicon atoms is the minimum is 1 to 10 atomic % [[,]] and is 0.3 to 0.8 times the content at a portion where the content of hydrogen atoms and/or halogen atoms is the maximum.

Please amend the paragraph starting at page 32, line 7, and ending at page 32, line 17, as follows:

Although the details of the mechanism are not clear, it is considered that when a an alloy semiconductor containing silicon atoms and germanium atoms is deposited, a difference arises in the electromagnetic wave energies acquired by each of the atoms due to the differences in ionization rates of the silicon atoms and germanium atoms, with the result that even if the content of the hydrogen and/or halogen in the alloy semiconductor is small, the relaxation proceeds sufficiently to provide a high quality alloy semiconductor.

Please amend the paragraph starting at page 33, line 13, and ending at page 33, line 27, as follows:

As the i-type semiconductor layer when the semiconductor element of the present invention is applied to a photovoltaic element, there can suitably be used, in addition to semiconductors with a uniform bandgap, those ~~semiconductor~~ semiconductors which contain silicon atoms and germanium atoms such that the bandgap changes smoothly in the direction of layer thickness of the i-type semiconductor layer, and that the minimum of the bandgap is offset from the central position of the i-type semiconductor

layer toward the interface between the p-type semiconductor layer and the i-type semiconductor layer. Further, a semiconductor layer doped with both a valency controller to be a donor and a valency controller to be an acceptor is also suitable as the i-type semiconductor layer.

Please amend the paragraph starting at page 35, line 11, and ending at page 35, line 15, as follows:

As the compounds which ~~contains~~ contain silicon atoms and are gasifiable, there are included, for example, SiH_4 , Si_2H_6 , Si_3H_8 , SiF_4 , SiHF_3 , SiH_2F_2 , SiH_3F , SiH_3Cl , SiH_2Cl_2 , SiHCl_3 , SiCl_4 , SiD_4 , SiHD_3 , SiH_2D_2 , SiH_3D , SiD_3F , SiD_2F_2 , $[\text{SiHD}_3]$, $\text{Si}_2\text{H}_3\text{D}_2$, etc.

Please amend the paragraph starting at page 35, line 16, and ending at page 35, line 20, as follows:

As the compounds which ~~contains~~ contain germanium atoms and are gasifiable, there are included, for example, germanium compounds such as GeH_4 , GeF_4 , GeHF_3 , GeH_2F_2 , GeH_3F , GeHCl_3 , GeH_2Cl_2 , GeH_3Cl , GeHD_3 , GeH_2D_2 , GeH_3D , GeD_4 , Ge_2H_6 , Ge_2D_6 , etc.

Please amend the paragraph starting at page 35, line 21, and ending at page 35, line 26, as follows:

As the compounds which ~~contains~~ contain carbon atoms and are gasifiable, there are included, for example, compounds represented by $\text{C}_n\text{H}_{2n+2}$ (n is an integer) such as

CH₄, etc., compounds represented by C_nH_{2n} (n is an integer) such as C₂H₂, etc., and CD₄, C₆H₆, CO₂, CO, or the like.

Please amend the paragraph starting at page 36, line 5, and ending at page 36, line 6, as follows:

The gases containing oxygen atoms include ~~gases as~~ O₂, CO, CO₂, NO, NO₂, N₂O, CH₃CH₂OH, CH₃OH, etc.

Please amend the paragraph starting at page 39, line 18, and ending at page 39, line 25, as follows:

The i-type semiconductor layer containing silicon atoms or germanium atoms formed by the ~~above-described~~ above-described deposited film formation method is such that there are less tail states on the valence band side even when the deposition rate is over 5 nm/sec, ~~and~~ that the tail states have an inclination of not more than 60 meV, and that the density of dangling bonds determined by the electron spin resonance (esr) is not more than 10¹⁷/cm³.

Please amend the paragraph starting at page 40, line 4, and ending at page 40, line 23, as follows:

In this example, a photovoltaic element was produced using the deposited film forming apparatus shown in Fig. 2. The deposition conditions of each of the semiconductor layers are shown in Table 1. The formation of the members such as electrodes in all the examples including this example and comparative examples was ~~made~~

~~following accomplished using~~ a conventional method. The microcrystalline semiconductor having a semiconductor junction within the same microcrystalline semiconductor of the present invention was used between the n-type semiconductor layer n1 and an i-type semiconductor layer i1 of the bottom photovoltaic element. After deposition of the n-type semiconductor layer n1, the n-type semiconductor layer n1 was irradiated with an excimer laser under the conditions shown in Table 2 in the loading chamber to ~~crystalize~~ crystallize the n-type semiconductor layer n1. Afterwards, the i-type semiconductor layer i1 was successively deposited on the n-type semiconductor layer n1 by the VHF plasma CVD method.

Please amend the paragraph starting at page 42, line 4, and ending at page 42, line 14, as follows:

When a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with a transmission electron microscope, it was confirmed for the photovoltaic elements of Example 1 that the region thought to be the boundary between the n-type semiconductor layer and the i-type semiconductor layer was constituted of microcrystal grains with a length in the layer thickness direction of 2000 - 4000 Å. Further, it was confirmed through secondary ion mass spectroscopy that the impurities (dopant) were localized on the substrate side of the microcrystal grains.

Please amend the paragraph starting at page 43, line 14, and ending at page 43, line 25, as follows:

Further, a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with an electron microscope and the amount of impurities was measured by secondary ion mass spectroscopy. As a result, it was confirmed for the photovoltaic element of Example 2 that a portion of each of the n-type semiconductor layer and the i-type semiconductor were formed within the same microcrystal grains. The shape of the microcrystal grains was columnar, the length in the layer thickness direction was 3000 Å, and the length in the direction perpendicular to the layer thickness direction was 300 Å.

Please amend the paragraph starting at page 45, line 13, and ending at page 45, line 22, as follows:

When a ~~cross-section~~ cross-section of the photovoltaic element of Example 4 was observed with an electron microscope, it was confirmed for i0 layer that uniform microcrystal grains were formed extending over the whole in the layer thickness direction in a layer thickness of 3000 Å. It was further confirmed through secondary ion mass spectroscopy that the implanted phosphorous atoms were distributed only on the substrate side, namely that a semiconductor junction was formed within a single microcrystal grain.

Please amend the paragraph starting at page 47, line 13, and ending at page 47, line 23, as follows:

When a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with a transmission electron microscope, it was confirmed for the photovoltaic elements of Example 5 that the region thought to be the boundary between the n-type semiconductor layer and the i-type semiconductor layer was constituted of

microcrystal grains 2000 - 5000 Å long in a film thickness direction. It was also confirmed through secondary ion mass spectroscopy that the impurities (dopant) were localized on the substrate side of these microcrystal grains.

Please amend the paragraph starting at page 49, line 26, and ending at page 50, line 21, as follows:

In this example, a photovoltaic element was produced using the deposited film forming apparatus shown in Fig. 2. The deposition conditions of each of the semiconductor layers are shown in Table 15. The formation of the members such as electrodes in all the examples including this example and comparative examples was ~~made following~~ accomplished using a conventional method. When depositing the bottom photovoltaic element, the input power was changed every 6 ~~second period~~ seconds between the numerical value in Table 15 and a numerical value 1.5 times that. The microcrystalline semiconductor having a semiconductor junction within the same microcrystalline semiconductor of the present invention was used between the n-type semiconductor layer n1 and an i-type semiconductor layer i1 of the bottom photovoltaic element. After deposition of the n-type semiconductor layer n1, the n-type semiconductor layer n1 was irradiated with an excimer laser under the conditions shown in Table 16 in the loading chamber to ~~crystallize~~ crystallize the n-type semiconductor layer n1. Afterwards, the i-type semiconductor layer i1 was successively deposited on the n-type semiconductor layer n1 by the VHF plasma CVD method.

Please amend the paragraph starting at page 52, line 1, and ending at page 52, line 11, as follows:

When a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with a transmission electron microscope, it was confirmed for the photovoltaic elements of Example 7 that the region thought to be the boundary between the n-type semiconductor layer and the i-type semiconductor layer was constituted of microcrystal grains with a length in the layer thickness direction of 2000 - 4000 Å. Further, through secondary ion mass spectroscopy, it was confirmed that the impurities (dopant) were localized on the substrate side of the microcrystal grains.

Please amend the paragraph starting at page 53, line 26, and ending at page 54, line 10, as follows:

Further, a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with an electron microscope and the amount of impurities was measured by secondary ion mass spectroscopy. As a result, it was confirmed for the photovoltaic element of Example 8 that a portion of each of the n-type semiconductor layer and the i-type semiconductor were formed within the same microcrystal grains. The shape of the microcrystal grains was columnar, the length in the layer thickness direction was 3000 Å, and the length in the direction perpendicular to the layer thickness direction was 300 Å.

Please amend the paragraph starting at page 56, line 7, and ending at page 56, line 16, as follows:

When a ~~cross-section~~ cross-section of the photovoltaic element of Example 10 was observed with an electron microscope, it was confirmed for i0 layer that uniform microcrystal grains were formed extending over the whole in the layer thickness direction in a layer thickness of 3000 Å. It was further confirmed through secondary ion mass spectroscopy that the implanted phosphorous atoms were distributed only on the substrate side, namely that a semiconductor junction was formed within a single microcrystal grain.

Please amend the paragraph starting at page 59, line 10, and ending at page 59, line 20, as follows:

When a ~~cross-section~~ cross-section of each of these photovoltaic elements was observed with a transmission electron microscope, it was confirmed for the photovoltaic elements of Example 11 that the region thought to be the boundary between the n-type semiconductor layer and the i-type semiconductor layer was constituted of microcrystal grains 2000 - 5000 Å long in the film thickness direction. It was also confirmed through secondary ion mass spectroscopy that the impurities (dopant) were localized on the substrate side of these microcrystal grains.

Please amend the paragraph starting at page 62, line 22, and ending at page 63, line 3, as follows:

Further, by the presence of microcrystal grains with different grain ~~diameters, it is~~ diameters makes it possible to make the distortion smaller than when filling three dimensional spaces (the semiconductor layer) with microcrystal grains with a uniform grain diameter. As a result, the transportability (mobility) of the photo-excited free carriers

within the microcrystalline semiconductor layer increases and the ~~life-time~~ lifetime of the carriers is extended.

Please amend the paragraph starting at page 87, line 2, and ending at page 87, line 12, as follows:

In a semiconductor element comprising microcrystalline semiconductor, a semiconductor junction is provided within a microcrystal grain. Further, in a semiconductor element comprising microcrystalline semiconductor, ~~providing~~ microcrystal grains of different grain diameters are provided as a mixture to from a semiconductor layer. Thereby, discontinuity of a semiconductor junction is ~~improved~~ lessened to thereby improve the characteristics, durability, and heat resisting properties of a semiconductor element. Distortion in a semiconductor layer is also reduced.